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(71) Applicants: THE TRUSTEES OF PRINCETON UNIVERSITY [US/US]; P.O. Box 36, Princeton, NJ 08544 (US). THE UNIVERSITY OF SOUTHERN CALIFORNIA [US/US]; The University of Southern California Park, Los Angeles, CA 90089 (US).

(72) Inventors: THOMPSON, Mark, E.; 4447 Pepper Creek Way, Anaheim Hills, CA 92807 (US). FORREST, Stephen, R.; 148 Hunt Drive, Princeton, NJ 08540 (US).

(74) Agents: MEAGHER, Thomas, F. et al.; Kenyon & Kenyon, One Broadway, New York, NY 10004 (US).

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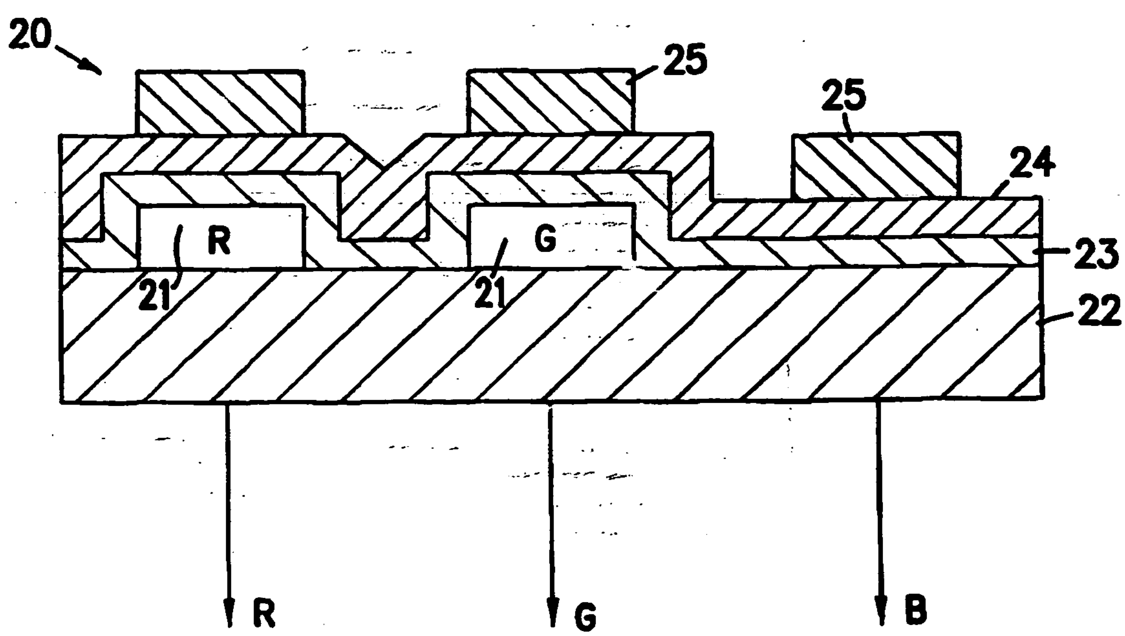
(54) Title: MULTICOLOR DISPLAY DEVICES



(57) Abstract

A multicolor display device includes a transparent substrate (22), red and green fluorescent dyes (21) ink jet printed onto the substrate, a conductive layer (23) deposited over the red and green dye, an organic blue light emitting layer (24) deposited over the conductive layer, and an electrical contact deposited onto the blue light emitting layer.

MULTICOLOR DISPLAY DEVICES

Field of the Invention

This invention relates to display devices, and more particularly to multicolor display devices having fluorescent dyes deposited by ink jet printing.

Background of the Invention

Display devices utilizing fluorescent media capable of absorbing light and emitting it at a longer wavelength are known. See, e.g., U.S. Patent No. 5,294,870 to Tang et al., entitled "Organic Electroluminescent Multicolor Image Display Device," the entire disclosure of which is hereby incorporated by reference. However, the fluorescent media in such devices are deposited using patterning techniques such as photolithography which are costly to perform. Hence, there exists a need for a method by which fluorescent media can be inexpensively and accurately deposited on a substrate to produce a multicolor display device.

Summary of the Invention

The present invention is directed to display devices, each comprising a substrate and fluorescent dye

substrate. The red and green light emitting regions are formed by ink jet printing red and green fluorescent dyes onto the substrate. No ink is deposited in the blue light emitting regions. Rather, the blue light emitting regions are left as empty spaces while the red and green fluorescent dyes are printed. After the red and green dyes are printed, a layer of transparent, conductive material is deposited over the red and green dyes and the empty spaces left for the blue light emitting regions. A layer of organic, blue light emitting device (OBLED) is thereafter deposited onto the layer of transparent, conductive material. Electrical contacts are then placed on the OBLED in each of the red, green and blue light emitting regions, to facilitate the application of voltage across the OBLED. The OBLED produces a blue emission in the blue light emitting regions, and further, stimulates fluorescent emission in the red and green light emitting regions thereby creating a luminous color display. In this embodiment, the red and green dyes preferably have strong absorption in the blue, and preferably further have high blue-to-red and blue-to-green conversion efficiencies.

In a further embodiment of the present invention, red, green and blue light emitting regions are ink jet printed in the form of pixels onto a transparent substrate. Each pixel has one of each of a red, green and blue light emitting region. This fourth embodiment is made in a manner similar to the third embodiment, the primary difference being that the light emitting regions of the fourth embodiment are arranged in tri-color pixels whereas the light emitting regions of the third embodiment are arranged in some predetermined configuration.

comes into contact.

The amount of host matrix is ordinarily selected to yield a viscosity compatible with the ink jet printing process and preferably ranges from about 2 to about 7 wt%. The amount of dye is selected such that it is present in an amount sufficient to give good color intensity, while not being so high that the dye molecules begin to aggregate reducing luminescence intensity. Preferred amounts of dye range from about 0.1 to about 6 wt% of the matrix.

In general, liquid inks of the present invention contain one or more dyes that fluoresce in red, green or blue, which are used to generate a luminescent region of the appropriate hue. The color of the luminescent region is dictated by the fluorescence energy of the dye and the relative proportions of the same. The dyes are preferably chosen to optimize the saturation (i.e., narrow lines at about 460, 520 and 650 nm for blue, green and red, respectively), giving a wide color range for the devices to be manufactured.

Preferred dyes with predominantly blue emission include: 8-anilino-1-napthalenesulfonic acid, 1,3-diphenyl-1,3-butadiene, diphenylhexatriene, Hoescht 33258, Hoescht 33324, thioflavin T, diamidino-2-phenylindole*2HCL, coumarin 152, coumarin 20, coumarin 2, coumarin 339, coumarin 1, coumarin 138, coumarin 102, coumarin 314, and coumarin 30.

Preferred dyes with predominantly green emission include: acridine orange, acridine yellow, acriflavin, dichlorofluorescene, 3,6-diaminoacridine, fluoresceneisothiocyanate, lucifer yellow, quinacrinerhodamine 123, quinacridone, dimethylquiancridone, fluorescene, rhodamine 110,

material that can be used as a hole transporter in OLEDs and has its maximum absorption in the UV part of the spectrum. The choice of matrix materials will depend, among other things, on the stability of the different materials under printing conditions, their ability to transmit the ultraviolet light that is used to fluoresce the dyes as well as the light produced by the dyes, and their ability to resist phase separation and stabilize the dyes with respect to aggregation.

The wavelength of the radiation used to fluoresce the dyes is preferably maximized to reduce its energy (and thus its tendency to degrade the display), but must be of greater energy than the light produced by the dyes. For this reason, the wavelength of the radiation is usually in the blue to near-UV range.

The substrate should be dimensioned such that it is flexible enough to accommodate its use in an ink jet printing device and should efficiently transmit ultraviolet radiation, visible radiation or both, depending on the application. The substrate preferably transmits visible and near ultraviolet radiation, while filtering out higher energy ultraviolet radiation. Preferred materials are flexible polyester and glass films (such as Pyrex™), with glass being more preferred due to its low oxygen permeability.

A first embodiment of the present invention is shown in Figure 1. In this embodiment, a luminous color display **(10)** is made by ink jet printing regions of fluorescent dye **(11)** onto the front surface of a substrate **(12)**. The front surface of substrate **(12)** is thereafter exposed to blue or UV radiation, thus stimulating fluorescent emission of dye **(11)**. The color of the dye region upon exposure can be controlled by

region.

Additional embodiments of the device structure of the present invention are constructed based on the arrangements shown in Figure 2. In these embodiments, red and green fluorescent dyes **(21)** are ink jet printed onto a transparent substrate **(22)** such as glass; a transparent, conductive layer **(23)** is deposited over the red and green dye; an organic blue light emitting device (OBLED) layer **(24)** is deposited over the transparent, conductive layer; and electrical contacts **(25)** are deposited onto the OBLED layer.

A preferred material for the transparent, conductive layer **(23)** is indium-tin oxide (ITO). One desirable property indium-tin oxide is its ability to filter out destructive, high energy ultraviolet radiation, while being transparent to visible and near-ultraviolet radiation.

Layer **(23)** can be formed by means of conventional sputtering or electron beam vapor deposition methods, and typically ranges in thickness from about 1000 to about 4000 Å. Below a certain thickness the resistance of the layer will begin to suffer, while above a certain thickness marginal utility becomes negligible. The deposition of layer **(23)** is preferably conducted under vacuum.

After conductive layer **(23)** is deposited, OBLED layer **(24)** is preferably deposited by thermal evaporation methods to a thickness which is often 400-1000Å. The ultimate thickness will depend upon the OBLED. Preferably, this thickness will be as thin as possible to lower the voltage of the device, without significantly compromising quantum efficiency. The deposition of layer

which are fluorescent in the solid state may be used for layer **(24)**. Examples of such polymers include poly(phenylene), and poly(N-vinylcarbazole).

Additional OLED materials are known in the art (see, e.g., U.S. Patent No. 5,294,870 to Tang et al., entitled "Organic Electroluminescent Multicolor Image Display Device"; Hosokawa et al., "Highly efficient blue electroluminescence from a distyrylarylene emitting layer with a new dopant," Appl. Phys. Lett., 67 (26) 25 December 1995, pp. 3853-3855; Adachi et al., "Blue light-emitting organic electroluminescent devices," Appl. Phys. Lett., 56 (9) 26 February 1990, pp. 799-801; Burrows et al., "Color-Tunable Organic Light Emitting Devices," Appl. Phys. Lett., Vol. 69, 11 November 1996, pp. 2959-2961). The entire disclosures of these references are hereby incorporated by reference.

Distyrylarylene derivatives such as those described in Hosokawa et al. are a preferred class of compounds. Other preferred OLEDs are described in the copending applications discussed below.

The deposition of electrical contacts **(25)** may be accomplished by vapor deposition or other suitable metal deposition techniques. A preferred method of depositing such contacts is by ink jet printing as disclosed, for example, in U.S. Patent Nos. 4,668,533, 5,132,248 and 5,266,098, the disclosures of which are hereby incorporated by reference in their entireties. These electrical contacts may be made from indium, platinum, gold, silver or combinations such as Ti/Pt/Au, Cr/Au or Mg/Ag. Mg/Ag contacts are preferred.

The embodiments discussed above in connection with Figure 2 have substantially the same device structure, the primary difference being that the light emitting

applications U.S. Serial Nos. 08/354,674; 08/613,207; 08/632,316; 08/632,322; 08/693,359; 60/010,013; and 60/024,001; and each is also herein incorporated by reference in its entirety.

The following Examples are merely illustrative of the present invention and are in no way intended to limit the scope of the present invention.

Example 1: Generating a passive picture to be back lit with UV.

In order to print a fluorescent image or pixel array with an ink jet printer or other ink delivery system, the inks are first prepared to match the optimal viscosity and other solution properties of the chosen printer. These inks consist of a carrier solvent, roughly 1-10 weight % matrix material and 0.001 - 0.05 weight % fluorescent dye. The dye is chosen to achieve a desired hue (typically red, green or blue) and the matrix material is chosen to give a stable film which supports the dyes and prevents aggregation. The three wells of the printer are charged with the red, green and blue inks. The image is printed directly onto a polymeric or glass substrate. The inks are mixed by the ink jet printer at each pixel, if needed to achieve the appropriate color. The brightness at each pixel is adjusted by varying the total amount of ink deposited at each pixel. A small amount of ink will allow most of the irradiating light to pass through the film giving very little visible light. A larger amount of ink deposited will give a significant absorbance and thus a relatively larger amount of visible light from dye fluorescence. The color of each pixel is strictly determined by the

organic multilayers are chosen to match the output of the OLEDs to the absorption spectra of the chosen red, green and blue dyes, and are well known to those skilled in the art of fabrication or organic light emitting devices. A mask is then applied and a film of a low work function metal is deposited above each pixel defined by the ink jet printer. Applying a bias between the conductive film and the metal electrode gives light which stimulates the dye region giving red, green and blue emission. The brightness at each pixel is controlled by setting the current level at the OLED. The color of a given pixel is controlled by the ratio of red to green to blue fluorescent dyes in the film.

Example 3. Generating a pixel array back lit with OBLEDs.

To print a fluorescent image or pixel array with an ink jet printer or other ink delivery system, the inks are first prepared to match the optimal viscosity and other solution properties of the chosen printer. These inks consist of a carrier solvent, roughly 1-10 weight % matrix material and 0.001 - 0.05 weight % fluorescent dye. The dye is chosen to achieve a desired hue (red and green) and the matrix material is chosen to give a stable film which supports the dyes and prevents aggregation. The wells of the printer are charged with the red and green inks. The image is printed directly onto a polymeric or glass substrate. The printer is used to deposit individual red and green fluorescent elements on the substrate. The thickness of the red and green fluorescent films are chosen to achieve a transparency of less than 10% at the intended irradiation wavelength. A layer of transparent conducting material is then applied

CLAIMS:

1. A display, comprising:

a transparent substrate;

fluorescent dye-containing material deposited in a dye layer onto said substrate by ink jet printing; and

a source of radiation for illuminating said fluorescent dye.

2. The display of claim 1, wherein

said substrate has a front side and a rear side, said substrate being transparent to ultraviolet radiation;

said fluorescent dye-containing material is provided on the front side of the substrate; and

said source is positioned to illuminate the rear side of the substrate.

3. The display of claim 1, wherein said substrate is transparent to visible radiation and said fluorescent dye-containing material is deposited onto said substrate in a pattern forming a plurality of light emitting regions, at least a portion of said light emitting regions comprising one or more fluorescent dyes selected from a red fluorescent

directly emits blue light in each of the blue light emitting regions, and said organic blue light stimulates the fluorescent dye in each of the red and green light emitting regions.

7. The display of claim 3, wherein said transparent, conductive layer comprises indium-tin oxide.

8. The display of claim 1, wherein said fluorescent dye-containing material comprises one or more fluorescent dyes and a matrix material.

9. The display of claim 8, wherein said dye is present in an amount ranging from about 0.1 to about 6 wt% relative to said matrix material.

10. The display of claim 8, wherein said matrix material is selected from polymethylmethacrylate, polyvinylcarbazole, polybutadiene, polyesters and N,N'-diphenyl-N,N'bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine.

11. The display of claim 1, wherein said substrate is selected from glass and polyester.

12. A method for creating a display, comprising the steps of:

providing a transparent substrate;

depositing an ink comprising a fluorescent dye onto said substrate, said depositing occurring by ink jet printing; and

forming an electrical contact in contact with said organic blue light emitting device.

15. The method of claim 14, wherein said light emitting regions comprise red, green and blue light emitting regions arranged in a predetermined configuration.

16. The method of claim 15, wherein said red, green and blue light emitting regions are arranged in pixels, each pixel comprising one red light emitting region, one green light emitting region and one blue light emitting region, and wherein said electrical contact contacts said organic blue light emitting device in each of said red, green and blue light emitting regions.

17. The method of claim 15 wherein each of said red light emitting regions comprises a red fluorescent dye region and each of said green light emitting regions comprises a green fluorescent dye region; and wherein said organic blue light emitting device directly emits blue light in each of the blue light emitting regions, and said organic blue light stimulates the fluorescent dye in each of the red and green light emitting regions.

18. The method of claim 12, wherein said ink comprises one or more fluorescent dyes, a matrix material and a liquid carrier medium.

19. The method of claim 18, wherein said ink comprises from about 2 to about 7 wt% matrix material.

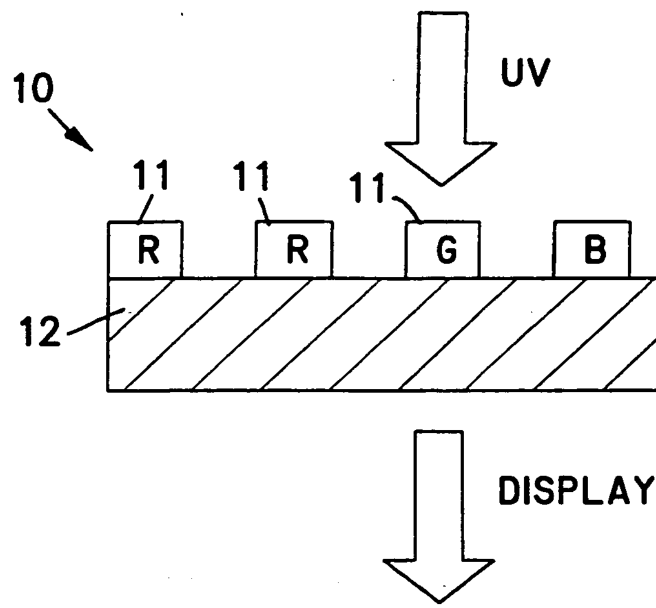


FIG. 1

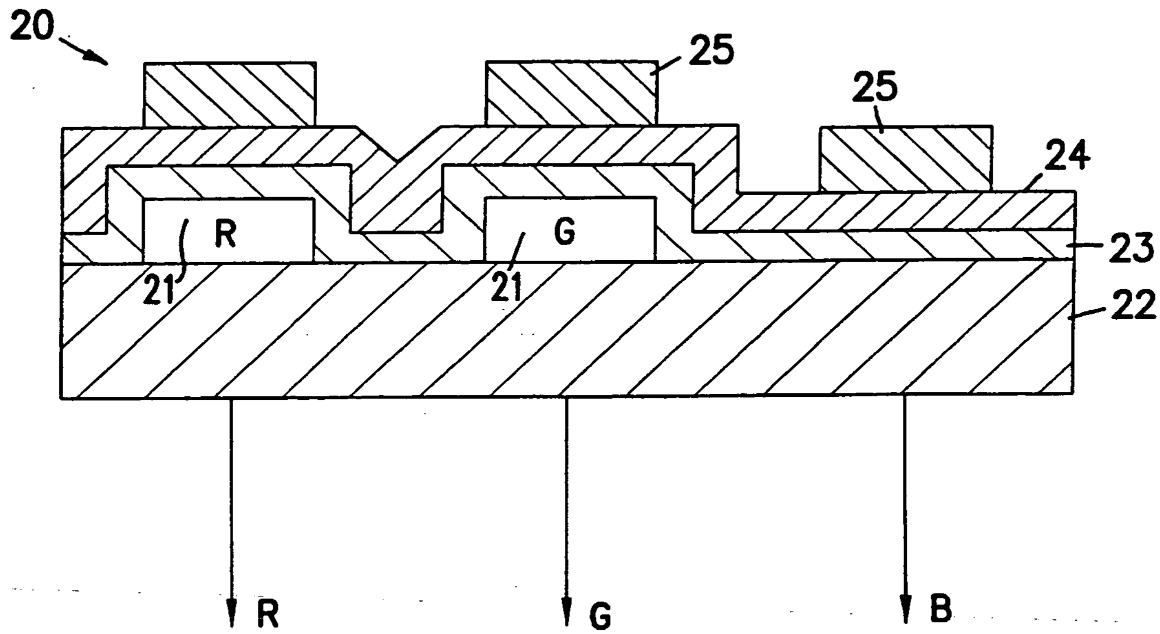


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/23635

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :HO5B 33/12
US CL :313/504,500,501,503,506,509; 428/917,690; 315/169.3
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 313/504,500,501,503,506,509; 428/917,690; 315/169.3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,294,870 A (TANG et al) 15 March 1994 (15.03.94), col. 13, lines 9-17, col. 31, line 50-col. 32, line 54, col. 36, lines 4-68.	1-22
X	US 4,769,292 A (TANG et al) 06 September 1988 (06.09.88c), col. 4, line 41-col. 5, line 68	1-22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
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Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer ASHOK PATEL
Facsimile No. (703) 305-3230	Telephone No. (703) 305-4950